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that phenylselenenic acid generated from syn elimination of the corresponding selenoxide is recycled during the electrolysis. Therefore, the electricity required for the total conversion is effectively saved.[15]

The effect of salts such as $MgSO_4$, $CaSO_4$ (82%), Na_2SO_4 (86%), K_2SO_4 (65%), $SrSO_4$ (51%), $BaSO_4$ (54%), and $Mg(ClO_4)_2$ (63%) is remarkable for the recycle, since the yield of **14** was only 26% in the absence of these salts and 10 mol % of diphenyl diselenide to **5** was employed. It is reasonable to assume that these salts prevent the conversion of phenylselenenic acid into inert phenylseleninic acid both by disproportionation[16] and in part by electrooxidation,[17] although the detailed mechanism of the effect is not yet clear.[18]

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(15) For instance, electrolysis of **5** in the presence of stoichiometric amount of diphenyl diselenide requires almost twice the amount of electricity (7.8 F/mol) in MeOH although the yield is slightly better (91% → 95%, Table I).

(16) (a) Behaghel, O.; Seibert, H. *Chem. Ber.* **1933**, *66*, 708. (b) Reference 11b.

(17) After electrolysis phenylseleninic acid was extracted with aqueous Na_2CO_3 and was converted into diphenyl diselenide by reduction with $NaHSO_3$.[2]

(18) A study on the mechanism of the recycle and the electrode process of diphenyl diselenide in the present electrolysis system is going on. The details will be reported elsewhere.

Stereomutation at Pentacoordinate Silicon by Intramolecular Ligand Exchange

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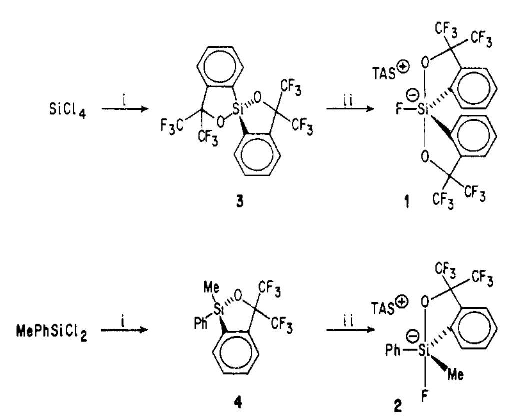
Although anionic, pentacoordinate silicon species have received some attention,[1] detailed studies describing both structure and ligand exchange processes have not been reported. We wish to present the first direct evidence for stereomutation of a pentacoordinate silicon compound by intramolecular ligand exchange.

The spiro siliconate **1**,[2] prepared by reaction of **3**[1a] with tris(dimethylamino)sulfonium (TAS) trimethyldifluorosiliconate[3] (Scheme I), exhibits a temperature-dependent ^{19}F NMR spectrum. The $A_3A_3'B_3B_3'X$ pattern observed in the limiting low-temperature spectrum (−15 °C) is transformed to a simple $A_{12}X$ pattern (at 70 °C) when interchange of diastereotopic trifluoromethyl groups is sufficiently rapid.[4] Visual fit of observed and calculated[5] spectra at various temperatures provided $\Delta G^\ddagger = 16.6$ kcal/mol ($\Delta H^\ddagger = 14.1$ kcal/mol; $\Delta S^\ddagger = -8$ eu) (Figure 1). Spectra were concentration independent and, except for minor differences in $\Delta\nu$, were solvent independent (acetonitrile, 1,2-dichloroethane). The exchange rate was unchanged by addition of either hexamethylphosphoramide or hexamethyldisilazane (HMDS).[6] That

Scheme I[a]



[a] (i) Dilithium reagent from hexafluorocumyl alcohol and 2 equiv of *sec*-butyllithium. (ii) $(Me_2N)_3S^+Me_3SiF_2^-$ in acetonitrile; TAS = $(Me_2N)_3S$.

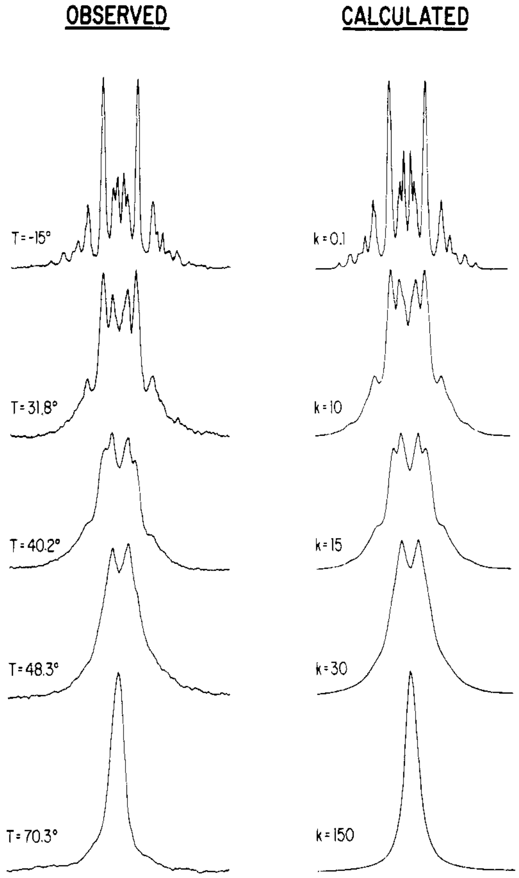


Figure 1. Representative observed and calculated ^{19}F NMR spectra for **1** (CF_3 region). Spectra were recorded while decoupling protons and the silicon-bound fluorine nucleus.

[†] Contribution No. 2904.

(1) (a) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591. (b) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155. (c) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 1167. (d) Corriu, R. J. P.; Royo, G.; De Saxcé, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892. (e) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 6973. (f) Boer, F. P.; van Remoortere, F. P. *Ibid.* **1970**, *92*, 801. (g) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1974**, 2051. (h) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480. (i) Breliere, C.; Carre, F.; Corriu, R. J. P.; De Saxcé, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, Cl. (j) Frye, C. L. *J. Am. Chem. Soc.* **1970**, *92*, 1205.

(2) mp 141–142 °C. Anal. Calcd for $C_{24}H_{26}N_3O_2F_{13}SSi$: C, 41.44; H, 3.77; N, 6.04. Found: C, 41.81; H, 3.84: N, 5.91. Molecular weight determined by osmometry in 1,2-dichloroethane was 650.

(3) Middleton, W. J. (to Du Pont) U.S. Patent 3 940 402. Tris(dimethylamino)sulfonium trimethyldifluorosiliconate was prepared according to the following procedure. Sulfur tetrafluoride (0.12 mol) was condensed in a flask charged with dry ether (150 mL). (Dimethylamino)trimethylsilane (0.37 mol) was added dropwise to the mixture at −78 °C. The mixture was warmed slowly to 25 °C and stirred for 72 h in an atmosphere of dry nitrogen. Filtration under nitrogen provided a nearly quantitative yield of white solid, mp 58–62 °C.

(4) **1**: ^{19}F NMR (−15 °C, CD_3CN) ϕ_A −74.80, ϕ_B −75.05, ϕ_X −130.1, J_{AB} = 9.2 Hz, J_{AX} ~3.5 Hz, J_{BX} ~1.5 Hz; (70 °C) ϕ_A −74.93, ϕ_X −130.1, J_{AX} = 2.5 Hz (13 line pattern).

(5) Spectra were calculated by using LAOCOON 3 and DNMR 3 programs. Kleier, D. A.; Binsch, G. "DNMR3: A Computer Program for the Calculation of Complex Exchange-Broadened NMR Spectra. Modified Version for Spin Systems Exhibiting Magnetic Equivalence or Symmetry," Program 165, Quantum Chemistry Program Exchange, Indiana University, 1970. See also: *J. Magn. Reson.* **1970**, *3*, 146.

(6) HMDS was added to remove trace amounts of water or acid which might be present.

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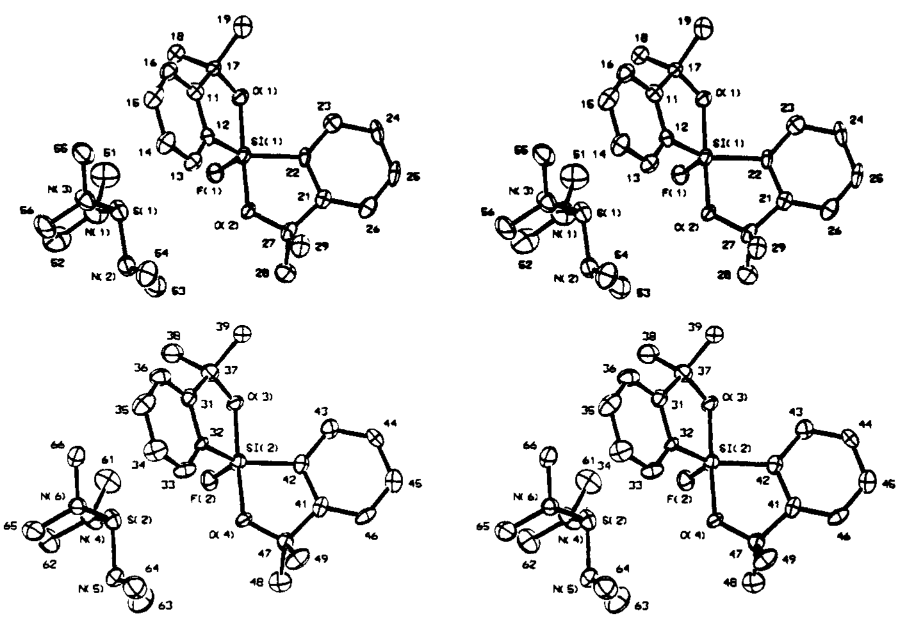

Figure 2. Stereodrawing of the two crystallographically independent ion pairs of **1** (F atoms on the CF_3 groups and H atoms are not shown).

the silicon-bound fluorine atom of **1** does not undergo exchange at a significant rate was confirmed by the ^{29}Si NMR spectrum (−76.58 ppm (d, J_{SiF} = 227 Hz))].[7]

An X-ray single-crystal diffraction study[8] of **1** shows that the salt consists of two crystallographically independent ion pairs which are geometrically similar (Figure 2). The ion-pair formation is accomplished through an electrostatic interaction between the coordinated fluorine atom and the sulfur atom of a neighboring cation.[9] The silicon atom is pentacoordinate with the fluorine and two carbon atoms forming the equatorial plane of a somewhat distorted trigonal bipyramid. It was suggested[10] that spirocyclic pentacoordinated compounds of silicon(IV) should adopt a square-pyramidal geometry. In the present case, where ring termini are different, it is not unreasonable that the silicon geometry is shifted toward the trigonal-bipyramidal form (δ_{24} = 43.2 and 41.6° for the two anions).[11]

The crystal structure of **1** provides a basis for interpreting the NMR data. The anion has approximate C_2 symmetry which is consistent with our observation of only two distinct trifluoromethyl groups. We consider the Berry pseudorotation process, amply demonstrated for other pentacoordinate metalloid centers,[12] to be the most reasonable enantiomerization mechanism for **1**. A topological graph is useful for visualizing the interconversions of trigonal-bipyramidal intermediates.[12b] Energy required for a ring spanning two equatorial positions would be offset in part by an equatorial-to-axial site change for the fluorine ligand. Ligand permutation by silicon–oxygen bond breaking steps is unlikely but cannot be strictly excluded. TAS siliconate **2** was therefore prepared[13] (Scheme I) as a structure incapable of enantiomerization by simple silicon–oxygen bond cleavage and recombination steps (see Table I).

Table I. Selected Bond Distances and Angles for 1

Bond Distances, Å			
Si(1)-F(1)	1.632 (3)	Si(2)-F(2)	1.631 (3)
Si(1)-O(1)	1.806 (4)	Si(2)-O(3)	1.792 (4)
Si(1)-O(2)	1.782 (4)	Si(2)-O(4)	1.787 (3)
Si(1)-C(12)	1.889 (5)	Si(2)-C(32)	1.869 (5)
Si(1)-C(22)	1.873 (5)	Si(2)-C(42)	1.883 (5)
S(1)-N(1)	1.609 (5)	S(2)-N(4)	1.602 (4)
S(1)-N(2)	1.687 (5)	S(2)-N(5)	1.692 (4)
S(1)-N(3)	1.607 (5)	S(2)-N(6)	1.621 (4)
S(1)-F(1)	3.205 (3)	S(2)-F(2)	3.143 (3)
Bond Angles, deg			
F(1)-Si(1)-O(1)	91.5 (2)	F(2)-Si(2)-O(3)	91.6 (2)
F(1)-Si(1)-O(2)	91.9 (2)	F(2)-Si(2)-O(4)	92.2 (2)
F(1)-Si(1)-C(12)	114.3 (2)	F(2)-Si(2)-C(32)	113.7 (2)
F(1)-Si(1)-C(22)	113.5 (2)	F(2)-Si(2)-C(42)	112.5 (2)
O(1)-Si(1)-O(2)	176.6 (2)	O(3)-Si(2)-O(4)	176.2 (2)
O(1)-Si(1)-C(12)	86.1 (2)	O(3)-Si(2)-C(32)	86.9 (2)
O(1)-Si(1)-C(22)	92.2 (2)	O(3)-Si(2)-C(42)	91.5 (2)
O(2)-Si(1)-C(12)	92.5 (2)	O(4)-Si(2)-C(32)	92.0 (2)
O(2)-Si(1)-C(22)	86.5 (2)	O(4)-Si(2)-C(42)	86.7 (2)
C(12)-Si(1)-C(22)	132.2 (2)	C(32)-Si(2)-C(42)	133.7 (2)
Si(1)-F(1)-S(1)	114.4 (1)	Si(2)-F(2)-S(2)	114.5 (1)
F(1)-S(1)-N(1)	101.4 (2)	F(2)-S(2)-N(4)	98.6 (2)
F(1)-S(1)-N(2)	104.3 (2)	F(2)-S(2)-N(5)	110.2 (2)
F(1)-S(1)-N(3)	131.7 (2)	F(2)-S(2)-N(6)	130.2 (2)
N(1)-S(1)-N(2)	100.4 (3)	N(4)-S(2)-N(5)	100.5 (2)
N(1)-S(1)-N(3)	114.9 (3)	N(4)-S(2)-N(6)	115.0 (3)
N(2)-S(1)-N(3)	199.5 (3)	N(5)-S(2)-N(6)	98.9 (2)

The low-temperature (23 °C) limiting ^{19}F NMR spectrum (propionitrile) of **2** exhibits uncoupled CF_3 [ϕ −74.16 and −75.19 (J = 9.5 Hz, A_3B_3)] and Si-F (ϕ −97.56) signals. The absence of spin coupling of the unique fluorine,[14] even in the presence of added HMDS[6] at −30 °C reveals that the fluorine ligand is un-

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(7) External Me_4Si was used as chemical shift standard.

(8) Crystal structure information: Monoclinic, space group $P2_1/c$; at −100 °C, a = 12.123 (2), b = 19.347 (3), c = 25.232 (4) Å; β = 90.67 (1)°; V = 5918 $Å^3$; Z = 8 (2 molecules per asymmetric unit). Syntex P3 diffractometer, graphite monochromator, Mo Kα, λ = 0.71069 Å, omega scans of 1.0°, $4 < 2\theta < 47°$, 8980 reflections. The structure was refined by full-matrix, least-squares techniques: 4667 reflections with $F_o^2 > 2\sigma(F_o^2)$, 857 variables (S, Si, F, O, N, and C with anisotropic thermal parameters, H's of anion with isotropic thermal parameters; H's of cation were calculated, not refined), R = 0.059, R_w = 0.043. The largest peak in the final difference map had a magnitude of 0.21 e $Å^{-3}$ and was located in the middle of the ring formed by Si(1), O(2), C(21), C(22) and C(27). The mathematical and computational details may be found in the following reference: Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

(9) The sulfur atom has approximate tetrahedral coordination when the fluorine atom is included in the coordination sphere. Two of the nitrogen atoms in the cation have greater sp^2 character than the third. These two nitrogen atoms have more nearly planar geometries (the third is clearly pyramidal) and have much shorter S–N bonds.

(10) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7972.

(11) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(12) For reviews and leading references, see: (a) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257. (b) Mislow, K. *Ibid.* **1970**, *3*, 321.

(13) The tetracoordinate precursor **4**, obtained after kugelrohr distillation, liquid chromatography (silica gel, 95:5 petroleum ether/ether), and recrystallization from petroleum ether at −78 °C, exhibited mp 60–62 °C; ^{19}F NMR ϕ −75.26 and −75.90 (J = 9.0 Hz, A_3B_3); ^1H NMR δ_{CDCl_3} 7.85–7.00 (m), 0.70 (s); ^{29}Si NMR +24.23 ppm.[7] Anal. Calcd. for $C_{16}H_{12}F_6OSi$: C, 53.04; H, 3.34. Found: C, 53.24; H, 3.31.

(14) Siliconate **2**: ^1H NMR δ_{CD_3CN} 8.10–7.95 (m, 1 H), 7.88–7.70 (m, 2 H), 7.58–7.00 (m, 6 H), 2.72 (s, 18 H), 0.14 (s, 3 H); ^{29}Si NMR −75.13 ppm (s); mol wt (determined by osmometry in 1,2-dichloroethane) 515.

dergoing very rapid exchange in a process which does not permute CF_3 groups. This result is confirmed by the averaged A_3B_3 pattern [ϕ −74.72 and −75.51, (J = 9.2 Hz)] observed in the ^{19}F NMR spectrum (CF_3 region) of an equimolar mixture of **2**/**4** (−25 °C). The trifluoromethyl groups in **2** exchange at elevated temperatures, with an estimated activation energy $\Delta G^{\ddagger}_{54}$ = 17.0 kcal/mol. Noticeable curvature appeared in the plot of ln k vs. $1/T$, and the accuracy of derived activation parameters is thereby reduced. We interpret the nonlinearity to indicate that at least two enantiomerization mechanisms are operating.[15] In contrast to the behavior of **1**, spectra of **2** are solvent dependent, and the exchange rate is sensitive to impurities. Addition of small amounts of HMDS[6] to propionitrile solutions of **2** reduced the CF_3 exchange rate and raised $\Delta G^{\ddagger}_{94}$ to ca. 19 kcal/mol.

The observation that the exchange rate of **1** is independent of solvent or added nucleophilic solvent militates against involvement of hexacoordinate silicon.[17] While enantiomerization of **2** cannot be accounted for by simple silicon–oxygen bond breaking steps, rapid exchange of the fluoride ligand may play a role in the itinerary for CF_3 exchange.

Acknowledgment. We thank Dr. G. S. Reddy and W. John for ^{19}F NMR data. Professor J. D. Roberts kindly supplied a copy of DNMR 3 which was adapted for use on our computer by Dr. R. M. Hilmer.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure amplitudes (47 pages). Ordering information is given on any current masthead page.

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[15] Many alternate mechanisms are possible and some may act in concert with pseudorotation. We note two which appear most reasonable: (1) An HF-catalyzed axial–equatorial exchange of the fluorine ligand; (2) axial loss coupled with edge attack on **4** (or equatorial loss coupled with face attack) of the rapidly exchanging fluorine ligand.[16]

[16] The lowest energy pathway for fluoride exchange is believed to involve axial loss and face attack. For calculations on model systems, see Wilhite, D. L.; Spialter, L. *J. Am. Chem. Soc.* **1973**, *95*, 2100. Paybutt, P. *Mol. Phys.* **1975**, *29*, 389.

[17] Such species have been implicated in the racemization of tetracoordinate silicon halides (Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1.) They were believed responsible for axial/equatorial site exchange in pentacoordinate silicon fluorides (Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 3845.)

Alkylation and Oxidative Dimerization of Enolate Anions by Radical Chain Processes[1]

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Received March 20, 1981

The radical chain involving reactions 1–3[2,3] has been termed

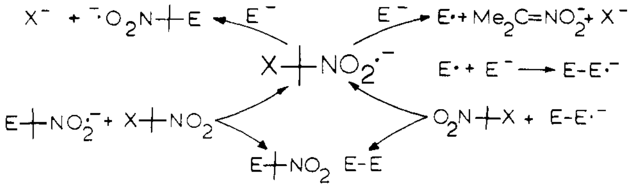
$$RX^{-}\cdot \rightarrow R\cdot + X^- \quad (1)$$

$$R\cdot + N^- \rightarrow RN^{-}\cdot \quad (2)$$

$$RN^{-}\cdot + RX \rightarrow RX^{-}\cdot + RN \quad (3)$$

$S_{RN}1$.[4] In such substitutions the possibility exists that reactions 1 and 2 may merge and that R· may not be an intermediate. A distinction between a concerted process and the consecutive reactions 1 and 2 can be made on the basis of competitive experiments. When two anions are allowed to compete for a series of substrates containing a common R moiety, the relative reactivities of the anions should be independent of the leaving groups only if free R· is an intermediate. This technique has been employed in aromatic $S_{RN}1$ reactions,[5] and for the reaction of $XCMe_2NO_2$ (X = Cl, NO_2, or p-$MePhSO_2$) with $Me_2C{=}NO_2^-$ and $MeC(CO_2Et)_2^-$ in Me_2SO.[6]

Scheme I. Bimolecular Substitution and Oxidative Dimerization



We now report a second type of competition in the reaction of easily oxidized monoenolate anions (E = $RC(O^-){=}CHR'$) with $XCMe_2NO_2$, leading to coupling (**1** and **2**) and symmetrical dimerization (**3**) products. Our results require that both processes 4 and 5 proceed by free radical chains and that the competition between these processes is determined by bimolecular reactions of $XCMe_2NO_2^{-}\cdot$ and not by reactions of free $O_2NCMe_2\cdot$.

$$E^-Li^+ + XCMe_2NO_2 \xrightarrow{THF} \underset{\mathbf{1}}{ECMe_2NO_2} + X^-$$
$$\mathbf{1} \xrightarrow{B^-} \underset{\mathbf{2}}{RCOC(R'){=}CMe_2} + NO_2^- \quad (4)$$

$$2E^-Li^+ + XCMe_2NO_2 \xrightarrow{THF} \underset{\mathbf{3}}{E\text{–}E} + X^- + Me_2C{=}NO_2^- \quad (5)$$

The competition between (4) and (5) for E^- = $PhC(O^-){=}CHR'$ with 2-chloro-2-nitropropane leads only to **1** and **2** with R′ = H and only to **3** with R′ = Ph. With R′ = Me, Et, or i-Pr both products **1** and **3** are observed. Increasing the steric bulk of R′ or the resonance stabilization of E· favors process 5. In all cases the presence of 5–10 mol % of $(t\text{-Bu})_2NO\cdot$ prevents the formation of **1**–**3**, and the starting phenone can be recovered. With R′ = Me or i-Pr the ratio **1**/**3** is unaffected by the presence of $Me_2C{=}NO_2Li$ in solvent mixtures of THF–hexane–Me_2SO (or HMPA). For these systems E· is trapped more readily by E^- than by $Me_2C{=}NO_2^-$. This is surprising since the addition step of reaction 6 must be more exothermic than the corresponding step of reaction 7. Apparently E· preferentially reacts with the anion which is the stronger base.[7]

$$E\cdot + Me_2C{=}NO_2^- \xrightarrow{slow} \mathbf{1}^{-}\cdot \xrightarrow{-e} \mathbf{1} \quad (6)$$

$$E\cdot + E^- \xrightarrow{fast} \mathbf{3}^{-}\cdot \xrightarrow{-e} \mathbf{3} \quad (7)$$

The ratio **1**/**3** from E^- = $PhC(O^-){=}CHR'$ or $Me_3CC(O^-){=}CH_2$ and $XCMe_2NO_2$ is independent of the concentrations of E^- or $XCMe_2NO_2$ but *depends strongly on the nature of X* with the ratio **1**/**3** decreasing from X = Cl to X = p-$MePhSO_2$ or NO_2 (Table I). A similar effect is observed for cyclohexanone enolate anion where $ClCMe_2NO_2$ yields >80% of the C-alkylation products, but $Me_2C(NO_2)_2$ yields mainly **3**.[8,9]

It is impossible to explain the variation in the ratio **1**/**3** from competition between reactions 8 and 9 or by competition between

$$Me_2\dot{C}\text{—}NO_2 + E^- \rightarrow ECMe_2NO_2^{-}\cdot \xrightarrow{-e} \mathbf{1} \quad (8)$$

$$Me_2\dot{C}\text{—}NO_2 + E^- \rightarrow Me_2C{=}NO_2^- + E\cdot \xrightarrow{E^-} \xrightarrow{-e} \mathbf{3} \quad (9)$$

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[1] Electron Transfer Processes. 27. This work was supported by Grant CHE-7823866 from the National Science Foundation.

[2] Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663; **1961**, *90*, 347. Russell, G. A.; Norris, R. K. Panek, E. J. *Ibid.* **1971**, *93*, 5839.

[3] Kornblum, N.; Michael, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660, 5662. Kornblum, N.; Boyd, S. R.; Stuchal, F. W. *Ibid.* **1970**, *92*, 5783. Kornblum, N. K.; Boyd, S. D. *Ibid.* **1970**, *92*, 5784.

[4] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

[5] Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1979**, *102*, 6137.

[6] Russell, G. A.; Ros, F.; Mudryk, B. *J. Am. Chem. Soc.* **1980**, *102*, 7601.

[7] Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 3531.

[8] Russell, G. A.; Jawdosiuk, M.; Ros, F. *J. Am. Chem. Soc.* **1979**, *101*, 3379.

[9] In THF–hexane–HMPA (53:34:13) at −35 °C for 1 h, cyclohexanone enolate and $ClCMe_2NO_2$ yield 67% of **1**, 15% of **2**, and 11% of **3**.

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